DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

Preliminary geochemical study of ash-flow tuffs in the Morococala and Los Frailes volcanic fields, central Bolivian tin belt

By

George E. Ericksen[1], Robert L. Smith[1], Robert G. Luedke[1]
Mario Flores[2], Alfredo Espinosa[2],
Fernando Urquidi B[3], and Fernando Saravia[4]

Open-File Report 85-258

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature.

[1]Reston, Virginia
[2]GEOBOL, La Paz
[3]American Embassy, La Paz
[4]COMIBOL, La Paz

1985

CONTENTS

ILLUSTRATIONS

ABSTRACT

A preliminary geochemical study was made to test for unusual concentrations of tin and related elements in tuffs of the Morococala and Los Frailes volcanic fields, which cover part of the central Bolivian tin belt. These fields consist of sequences of predominantly quartz latitic ash-flow tuff sheets and minor andesitic to dacitic lavas. The volcanic rocks have radiometric ages of 8-6 m.y., and are younger than the subvolcanic intrusions (23-12 m.y.) with which most of the known tin and other metalliferous deposits of this region are associated. Characteristic trace-element concentrations were determined for what are assumed to be typical tuff sheets representative of both fields; tin values range from 1 to about 7 ppm. A few tuffs, however, contain diverse values for certain elements that perhaps indicate originally unusual concentrations in the magmas. Our preliminary data do not permit further evaluation of the tin potential of the Morococala and Los Frailes volcanic fields, but do suggest the possibility of associated tin deposits at depth in the caldera source areas.

INTRODUCTION

This report is concerned primarily with an evaluation of the trace-element compositions of unaltered quartz latitic ash-flow tuff sheets that cover part of the central Bolivian tin belt, and is based on analyses of part of a suite of samples collected during field work in 1982. These samples show relatively uniform trace-element contents, that are believed to represent characteristic geochemical background values with which other samples of tuff sheets with more variable trace-element contents can be compared. Other samples collected in 1982 have more diverse values of certain elements, such as lithium and tin, that indicate unusal concentrations of those elements in parts of the magma chamber.

The central and most productive part of the Bolivian tin belt in the eastern Andean cordillera (fig. 1) is covered by late Miocene (8-6 m.y.) volcanic rocks, chiefly peraluminous quartz latites, of presumed post-tin mineralization. These rocks predominate in two upland areas, the Morococala plateau in the north (fig. 2), having an area of about 1,500 km^2, and the larger 8,500 km^2 Los Frailes plateau in the south. It is estimated that the volcanic rocks in these two areas and in nearby satellite areas of more restricted extent cover about 35 percent of the central tin belt in which the known deposits show K/Ar ages of 23-12 m.y. Several of the largest tin deposits of Bolivia -- Llallagua, Huanuni, and Potosi -- are at or near the margins of the younger volcanic areas, and other mineral deposits (tin, silver, lead, zinc, and antimony) are found in windows of older rocks within these areas. The only known mineral occurrences in the younger (8-6 m.y.) volcanic rocks include scattered small deposits of wood tin, uranium, and antimony.

It has been speculated that tin deposits, perhaps comparable in size and grade to the largest deposits now known, may occur in the rocks hidden beneath the volcanic cover of the Morococala and Los Frailes areas. But it is also probable that the post-tin volcanic complexes of these areas, particularly in intracaldera areas, may have associated intrusions and related tin deposits. Our investigations of the geochemistry of the volcanic rocks are aimed at evaluating the potential for such mineralized

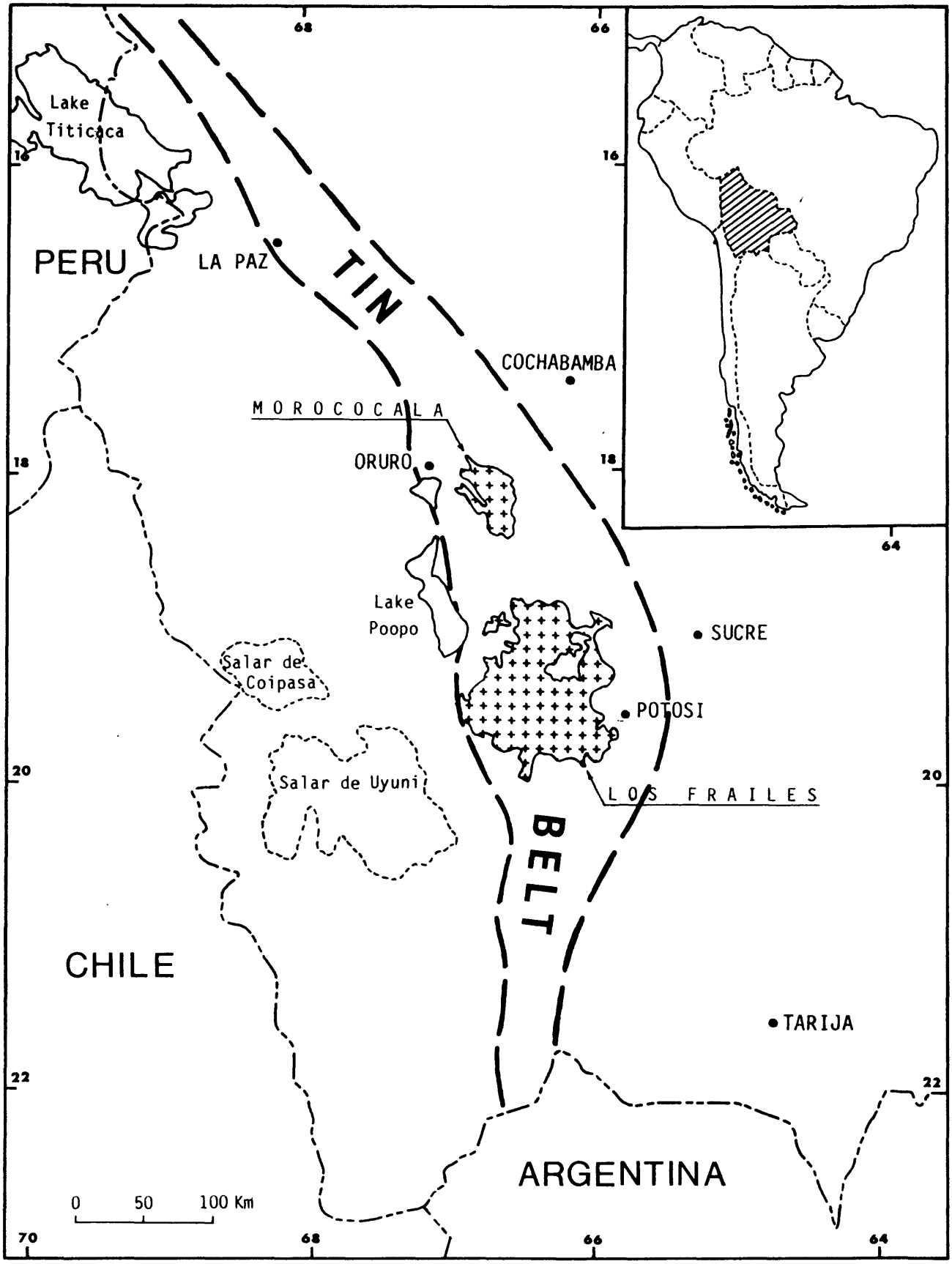

Figure 1. Location map showing Bolivian tin belt and the Morococala and Los Frailes volcanic fields

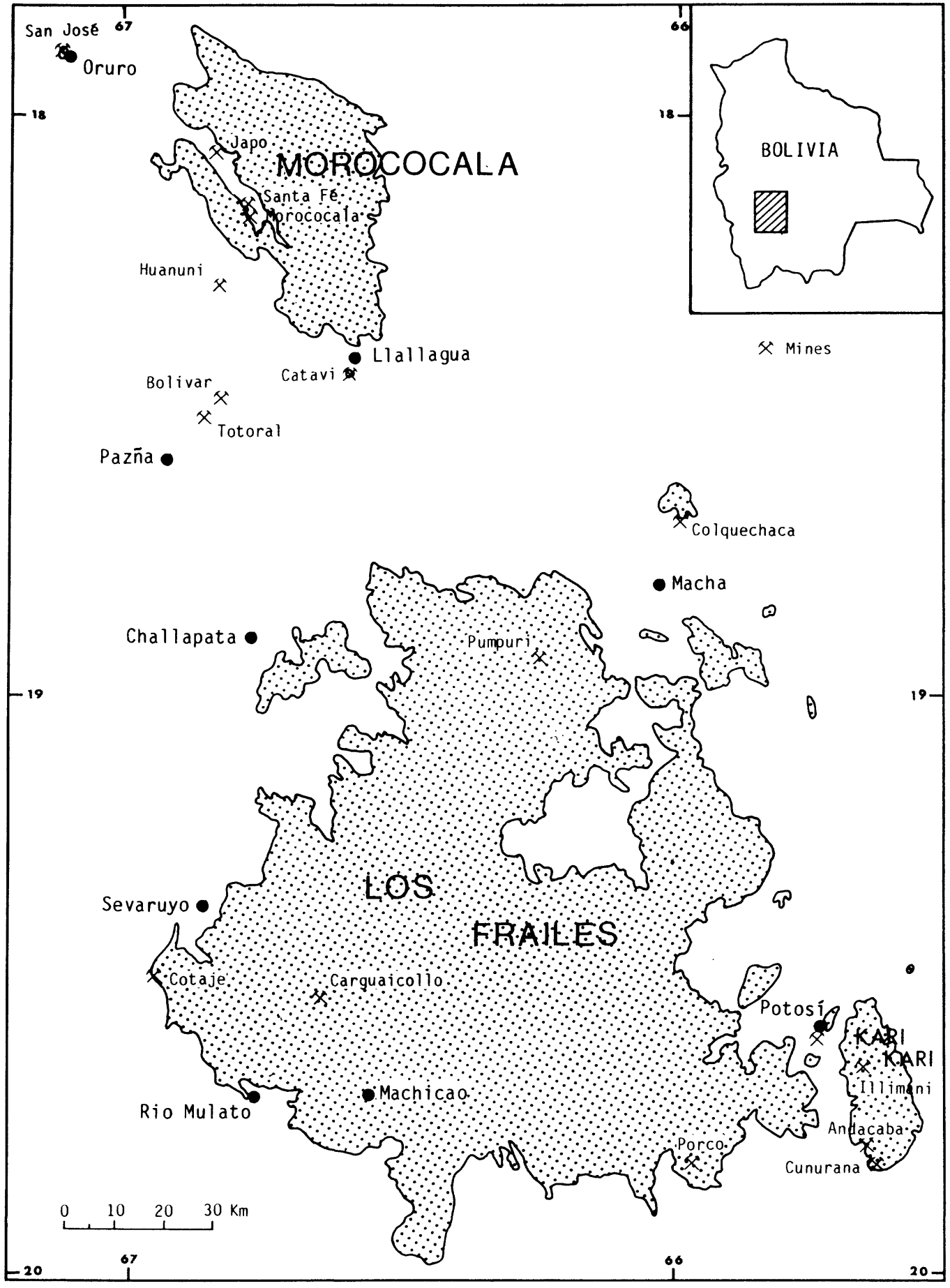

Figure 2. Geologic sketch map showing distribution of intrusive and extrusive rocks and principal mines of the Morococala-Los Frailes region

localities. They supplement investigations of a joint United Nations/GEOBOL (Servicio Geologico de Bolivia) study (Proyecto Cordillera; Convenio BOL/80/003) for evaluating the potential for tin deposits beneath the Morococala and Los Frailes volcanic fields (J. McNamme and others, unpublished data, 1982).

The current study of the geochemistry of the Morococala and Los Frailes volcanic fields, which is being carried out jointly by GEOBOL, COMIBOL (Compania Minera de Bolivia), and the USGS, is an outgrowth of a GEOBOL/USGS reconnaissance study of rhyolitic volcanic rocks in southern Bolivia concerned with determining the source of lithium now concentrated in salar brines of the region. That work resulted in discovery of a number of resurgent calderas that were the sources of the extensive ash-flow tuffs region (Davis and others, 1982). Several of the samples collected during that study proved to be unusually high in lithium and a few were high in tin.

The joint study to evaluate the tin potential of the young volcanic complexes was organized under the sponsorship of the IUGS (International Union of Geological Sciences), and a reconnaissance study was carried out in November 1982. Standard analytical work on samples collected at that time, still not complete, includes INAA (Instrumental Neutron Activation Analysis) trace-element and XRF (X-Ray Fluorescence) whole rock determinations. In addition, special chemical analyses for selected elements and semiquantitative spectrographic analyses of selected samples were made. Radiometric age determinations for several samples are being made.

The reconnaissance sampling and analytical work to date are not sufficiently detailed to allow unequivocal estimates of geochemical parameters and trends, but the majority of the samples, collected widely throughout the two areas and from various stratigraphic levels, show relatively uniform trace-element concentrations that we assume to represent the range of characteristic background geochemical values for these tuffs. However, a number of samples have relatively diverse values of trace-element concentrations for which the meanings are not yet clear.

GEOLOGIC SETTING

Recent geologic investigations (Sillitoe and others, 1975; Grant and others, 1980; J. McNamme and others, unpublished data, 1982) and radiometric age dating (Evernden and others, 1977; Grant and others, 1979) have clarified the history of Cenozoic magmatism in the central and southern Bolivian Andes. Those investigations showed that the intrusive and extrusive rocks of this region were emplaced during three stages: (1) early and middle Miocene (23-12 m.y.), (2) late Miocene (8-6 m.y.), and (3) late Pliocene-Pleistocene(?) (3.5 and less m.y.).

The subvolcanic dacitic to rhyodacitic porphyry intrusions with which most of the known major tin and other metalliferous deposits of this region are associated were emplaced during the first stage (23-12 m.y.). These intrusions cut a basement complex consisting of a thick sequence of folded and faulted Lower Paleozoic (Ordovician, Silurian, Devonian) marine clastic sedimentary rocks and, locally, inliers of Mesozoic (Cretaceous) and some Cenozoic (Miocene?) continental sedimentary and volcanic rocks. Among the

more important intrusions and associated major tin deposits, which have been dated radiometrically, are: Colquechaca stock (22-21 m.y.), Salvadora stock (21-20 m.y.) near Llallagua, San Pablo stock (21-20 m.y.) near Japo, and the stock (14-13 m.y.) near Potosi. Volcanic rocks of this stage, of which only remnants of former more extensive fields are preserved, consist of andesitic to rhyodacitic air-fall tuffs, lava flows, and ash-flow tuffs. These rocks are most widely exposed in the Kari Kari area (22-21 m.y.), formerly thought to be a granodiorite batholith and now recognized as a major Andean resurgent caldera (Francis and others, 1981). In addition to the important mineral deposits associated with the intrusive masses, a few metalliferous deposits occur locally in some of the volcanic rocks of this early stage.

The rocks of the Morococala and Los Frailes volcanic fields and a few small satellitic fields consist predominantly of a sequence of silicic nonwelded to welded ash-flow tuff sheets that were emplaced during the second stage of magmatic activity (8-6 m.y.). These tuffs unconformably overlie the basement complex, and are related to major caldera eruptive centers in each field. Individual tuff sheets are variable in thickness but probably average less than 100 m. The generally light to medium gray tuffs are commonly crystal rich, having prominent phenocrysts of biotite, quartz, and two feldspars in a glassy to devitrified matrix. These tuffs are all peraluminous and some have, in addition to the previously named phenocrystic minerals, the common peraluminous minerals of andalusite, cordierite, and muscovite. The tuffs probably range in composition from dacite to rhyolite but most are quartz latite with a range of 65 to 69 weight percent SiO_2.

Volcanic rocks of the youngest magmatic stage (3.5 m.y. and less) include local centers of andesitic to quartz latitic dome-flow complexes in the southern part of the Los Frailes volcanic field from near the western margin of the field to near the eastern margin. Some of these volcanic centers show little erosion and were probably active during Pleistocene time. A few of these centers have associated fumarolic activity and/or thermal springs. One such thermal spring near Machicao on the southwestern margin of the Los Frailes field is actively depositing the antimony mineral stibnite.

GEOCHEMISTRY

The discussion of geochemistry is concerned primarily with trace-element concentrations of a suite of 16 samples of ash-flow tuffs, of which 7 samples are from the Morococala volcanic field and 9 from Los Frailes. These samples show relatively uniform values for trace-element concentrations, for the volcanic fields both singlely or combined, that are considered to be typical for the late Miocene ash-flow tuffs of this region. Ranges and means of these values are shown in figure 3, and, for purpose of comparison, also the values of these same elements for the Bishop Tuff of eastern California (Hildreth, 1979) and the tuffs of Macusani of southern Peru (Noble and others, 1984). The Bishop Tuff consists of a sequence of ash falls and ash flows of high-silica rhyolite (75 percent SiO_2) that was emplaced during explosive activity of the Long Valley caldera about 0.7 m.y. ago. The detailed geochemical work of Hildreth (1977 and 1979) on the Bishop Tuff shows the changes in magma composition which 7 samples are from the Morococala volcanic field and 9 from Los

that may occur during a single caldera-forming eruption (indicated in figure 3 as early (E) and late (L) stages of the eruption). The Bishop Tuff was selected because it is a classic example of an ash-flow tuff (high-silica rhyolite) that shows extreme compositional variations that reflect trace-element zoning in the parent magma chamber. The tuffs of Macusani were selected for comparison because of their position at the north end of the Andean tin belt and because they are peraluminous and have exceptionally high concentrations of Sn (32-60 ppm) and Li (120-350 ppm) (Noble and others, 1984). These silicic tuffs appear to be the extrusive equivalent of tin-enriched two-mica granite.

The Morococala and Los Frailes tuffs differ from the Bishop Tuff (fig. 3) in having exceptionally high values (an order of magnitude higher) for Co, Th, and Eu and low values for Mo. In addition, Ba, Cr, Li, Sc, Zn, Zr, and Sm are significantly higher in the Bolivian tuffs than in the Bishop Tuff. The other trace-element contents shown in figure 3 have generally overlapping ranges. The Macusani tuffs (fig. 3), in contrast to the tuffs from the Morococala and Los Frailes valcanic fields, show exceptionally high values for Be, Cs, Li, Sn, and Ta, significantly higher values for Rb, U, and Zn, and significantly lower values for Ba, Hf, Sc, Th, and Zr.

Hildreth (1979) pointed out for the Bishop Tuff that with increasing temperature of the magma there is progressive enrichment of light rare-earth elements (LREE) and depletion of the heavy rare-earth elements (HREE) as well as a decrease in an initially large negative Eu anomaly. In figure 3 the late-stage (L) tuff, which formed from hotter magma from deeper in the magma chamber, shows enrichment in the LREE, a smaller Eu anomaly, and depletion of HREE relative to the early-stage (E), which formed from cooler magma from higher in the magma chamber. The rare-earth elements in the Morococala and Los Frailes tuffs are remarkably similar except that the Los Frailes tuffs do have a small negative Eu anomaly whereas the Morococala tuffs have almost none. The Bolivian tuffs possibly were slightly more depleted in HREE than the Bishop Tuff.

Of the elements determined by the analyses, tin was of particular interest, and is the only element given further attention in this preliminary paper. The unaltered quartz latitic ash-flow tuffs of the Morococala and Los Frailes volcanic fields shown in figure 3 have tin values ranging from 1 to about 7 ppm, with an average of 3.0 ppm. However, ash-flow tuffs from the Morococala field average about twice as much tin as those from the Frailes field. The 7 samples of Morococala tuff range in values of 1.8-6.7 ppm Sn, with a mean value of 4.3 ppm, whereas the 9 samples of Los Frailes tuffs range in values of 1-2.7 ppm Sn, with a mean value of 1.9 ppm. A few samples of unaltered Morococala and Los Frailes tuffs, not included in the above-mentioned ranges, have still higher tin values (10-20 ppm Sn), and may indicate magmas that as high-level intrusions might have formed lode-tin deposits. In a sequence of caldera-related volcanic rocks such as these, mapping of the distribution of the tin-anomalous tuff sheets may serve to locate source areas where such intrusions might occur at depth.

CONCLUSIONS

Inasmuch as the rocks of the Morococala and Los Frailes volcanic fields are younger than most of the known metalliferous deposits of the

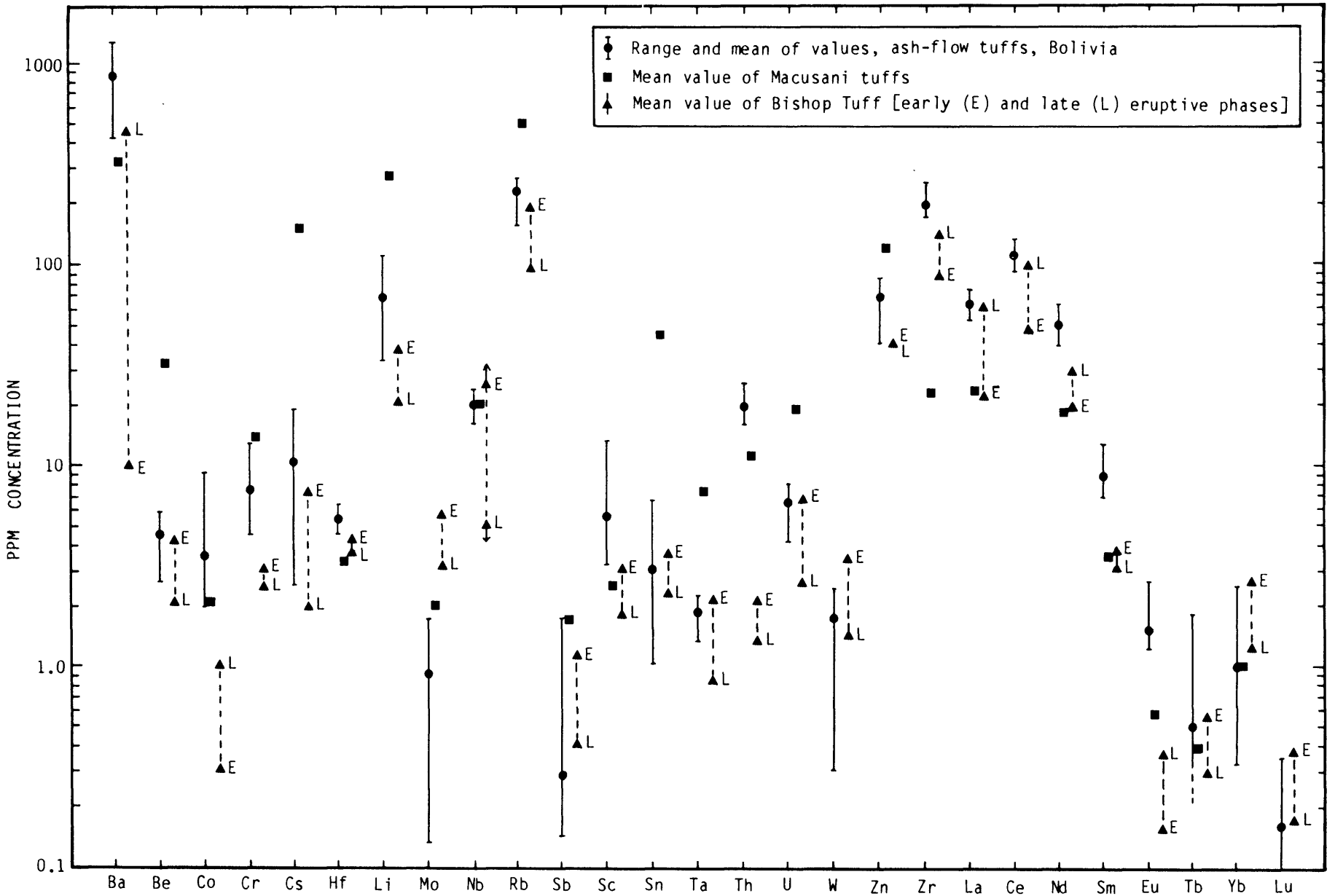

Figure 3. Trace-element values of representative ash-flow tuffs of the Morococala and Los Frailes volcanic fields, Bolivia, compared with selected ash-flow tuffs from the western U.S. and southern Peru

region, it is speculated that such deposits, including tin deposits, may occur beneath the volcanic cover. These deposits, which are associated with subvolcanic intrusions into Paleozoic clastic sedimentary rocks perhaps could be located by geophysical or geochemical prospecting methods, particularly in areas of relatively thin volcanic cover.

Our preliminary geochemical data for ash-flow tuffs in the Morococala and Los Frailes volcanic fields show tin values in the range of 1-7 ppm. However, a few tuffs show higher values of tin (10-20 ppm) that suggest a tin-enriched magma. If such magmas did exist during formation of the volcanic complexes of these areas, it is possible that some were emplaced as high-level intrusions having associated lode tin deposits.

REFERENCES CITED

Davis, J. R., and others, 1982, Progress report on lithium-related geologic investigations in Bolivia: U.S. Geological Survey Open-File Report OF 82-782, 14 p.

Evernden, J. F., Kriz, S. J., and Cherroni M, Carlos, 1977, Potassium-argon ages of some Bolivian rocks: Economic Geology, v. 72, p. 1042-1061.

Francis, P. W., Baker, M. C. W., and Halls, Christopher, 1981, The Kari Kari caldera, Bolivia, and the Cerro Rico stock: Journal of Volcanology and Geothermal Research, v. 10, p. 113-124.

Grant, J. N., Halls, Christopher, Avila S, Waldo, and Snelling, N. J., 1977, K-Ar ages of igneous rocks and mineralization in part of the Bolivian tin belt: Economic Geology, v. 74, p. 838-851.

Grant, J. N., Halls, Christopher, Sheppard, S. M. F., and Avila, Waldo, 1980, Evolution of the porphyry tin deposits of Bolivia: Mining Geology Special Issue, no. 8, p. 151-173.

Hildreth, E. W., 1977, The magma chamber of the Bishop Tuff: Gradients in temperature, pressure, and composition: University of California, Berkeley, Ph. D. Dissertation, 328 p.

_____ 1979, The Bishop Tuff; evidence for the origin of compositional zonation in silicic magma chambers in Chapin, C. E., and Elston, W. E., eds., Ash-flow tuffs: Geological Society of America Special Paper 180, p. 43-75.

Noble, D. C., and others, 1984, Rare-element-enriched, S-type ash-flow tuffs containing phenocrysts of muscovite, andalusite, and sillimanite, southeastern Peru: Geology, v. 12, p. 35-39.

Sillitoe, R. H., Halls, Christopher, and Grant, J. N., 1975, Porphyry tin deposits in Bolivia: Economic Geology, v. 70, p. 913-927.